

Dynamics of hydrogen in $\text{Pr}_2\text{Fe}_{17}\text{H}_4$ and $\text{Pr}_2\text{Fe}_{17}\text{H}_5$ studied by quasielastic neutron scattering

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Abstract

Quasielastic neutron scattering (QENS) has been used to investigate the dynamics of hydrogen in $\text{Pr}_2\text{Fe}_{17}\text{H}_4$, where isolated hexagons formed by the interstitial tetrahedral (t) sites of the metal lattice host mobile hydrogen atoms (on average, one H atom per hexagon). An activation energy of 0.10 eV has been measured for a localized jump process involving the hopping of these hydrogen atoms among adjacent vertices of each hexagon. This activation energy is somewhat lower compared to that for hydrogen hopping in $\text{Pr}_2\text{Fe}_{17}\text{H}_5$, where each hexagon is occupied by two hydrogen atoms. The fraction of the hydrogen atoms immobilized on the t sites by defects in the host metal lattice is slightly higher in $\text{Pr}_2\text{Fe}_{17}\text{H}_4$ compared to $\text{Pr}_2\text{Fe}_{17}\text{H}_5$. These results are consistent with our earlier view of $\text{Pr}_2\text{Fe}_{17}\text{H}_5$ as a system where the hopping of the t-site hydrogen atoms occurs through the correlated jumps of the two H atoms occupying each isolated hexagon.

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1. Introduction

A dramatic increase in Curie temperature and magnetization resulted from insertion of small atoms such as hydrogen into the host metal matrix of R_2Fe_{17} makes these materials attractive candidates for hard magnet materials [1–3]. Among them, one of the most promising compounds is $\text{Pr}_2\text{Fe}_{17}\text{H}_x$, which has been extensively studied [4–7]. Similar to other R_2Fe_{17} compounds with the lighter rare-earth atoms, $\text{Pr}_2\text{Fe}_{17}$ crystallizes in the $\text{Th}_2\text{Zn}_{17}$ rhombohedral $\bar{R}3m$ structure [8]. In the course of hydrogenation of $\text{Pr}_2\text{Fe}_{17}$, the host metal structure is retained, while an anisotropic increase of the lattice parameters occurs. Initially, hydrogen atoms in $\text{Pr}_2\text{Fe}_{17}\text{H}_x$ fill the interstitial 9e distorted octahedral (o) sites, with four Fe atoms and two Pr atoms at the corners [9], and at $x=3$, all these o sites become populated. Further hydrogenation leads to filling the interstitial 18g tetrahedral (t) sites, with two Fe atoms and two Pr atoms at the corners [8]. The t sites form arrays of isolated hexagons in

the basal plane of the hexagonal structure normal to the c -axis, with a side dimension of ≈ 1.16 Å, and a separation between the hexagons' centers of ≈ 8.70 Å, equal to the lattice constant a (see Fig. 1). The small size of the hexagons explains why the maximum hydrogen uptake in $\text{Pr}_2\text{Fe}_{17}\text{H}_x$ corresponds to $x=5$. In this case, one-third of the available t sites in the $\text{Pr}_2\text{Fe}_{17}$ host structure are filled. As proposed by Isnard et al. [3], a pair of hydrogen atoms occupies two diametrically opposed vertices of the hexagons in order to comply with Switendick's empirical criterion of ≈ 2.1 Å minimum H–H separation in ordered metal hydrides. Such a minimum has been ascribed to a repulsion interaction [10]. All but the opposite vertices of these hexagons in $\text{Pr}_2\text{Fe}_{17}\text{H}_5$ are separated by less than 2.1 Å.

Our earlier study [11] has revealed the dynamics of t-site hydrogen in $\text{Pr}_2\text{Fe}_{17}\text{H}_5$ due to the localized hopping of H atoms within the isolated hexagons. While such a hopping was previously observed in non-stoichiometric Laves phase compounds [12–15], it was surprising to see it in $\text{Pr}_2\text{Fe}_{17}\text{H}_5$, where the repulsive interaction between the two H atoms populating a hexagon might be expected to hinder the jumps. We have suggested that the jumps of these two H atoms must be correlated (that is, the simultaneous jumps of two atoms in the same direction must

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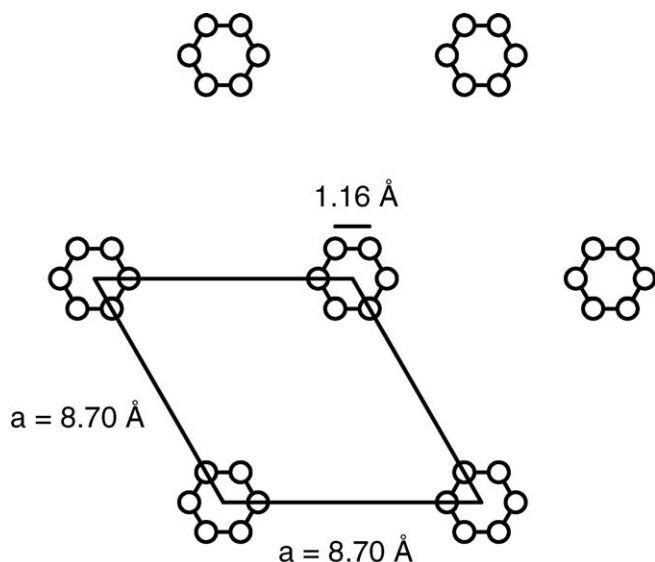


Fig. 1. Arrays of hexagons formed by the tetrahedral sites in the basal plane of $\text{Pr}_2\text{Fe}_{17}$.

occur) in order to reconcile the dynamics of hydrogen hopping in $\text{Pr}_2\text{Fe}_{17}\text{H}_5$ with the Switendick criterion of minimal hydrogen separation distance.

In order to study the effect of hydrogen occupation of the t-site hexagons on the hopping dynamics, we have extended our work in the current paper to include the compound with a composition of $\text{Pr}_2\text{Fe}_{17}\text{H}_4$. In this case, each isolated t-site hexagon contains, on average, only one hydrogen atom, and one may expect the absence of a second hydrogen atom to have a significant impact on the hopping dynamics.

2. Experimental details

The synthesis procedure for $\text{Pr}_2\text{Fe}_{17}$ samples has been described elsewhere [7,16,17]. Hydrogen was loaded by means of gas absorption. Neutron scattering experiments were carried out on the high flux backscattering spectrometer (HFBS) [18] at the NIST Center for Neutron Research. The HFBS provides $\approx 1 \mu\text{eV}$ energy resolution and the dynamic range of up to $\pm 35 \mu\text{eV}$ at a fixed final wavelength of 6.27 \AA . The sample was placed in an annular Al sample holder in a He atmosphere, sealed with an indium o-ring, and mounted onto a closed cycle refrigerator. The thickness of the sample was chosen to ensure 90% neutron transmission and thus minimize multiple scattering. The temperature of the refrigerator was controlled within $\pm 1 \text{ K}$. The data were collected at 260, 240, 220, 200, and 5 K. The spectrum measured at 5 K was used as the resolution function. The spectra collected at nine detectors covering the range of the scattering vectors $0.87 \text{ \AA}^{-1} < Q < 1.68 \text{ \AA}^{-1}$ (at the elastic channel) were used in the data analysis.

3. Results and discussion

Examples of the QENS spectra are shown in Fig. 2. The low-temperature data, which show no quasielastic signal, are used as the resolution function. The general trend is that the QENS broadening increases with temperature, indicating faster hopping (i.e. shorter time between jumps). Since hopping between well-separated hexagons is unlikely, we fit the QENS data with a model scattering function describing a hopping between the six sites of an isolated hexagon. The model scattering function

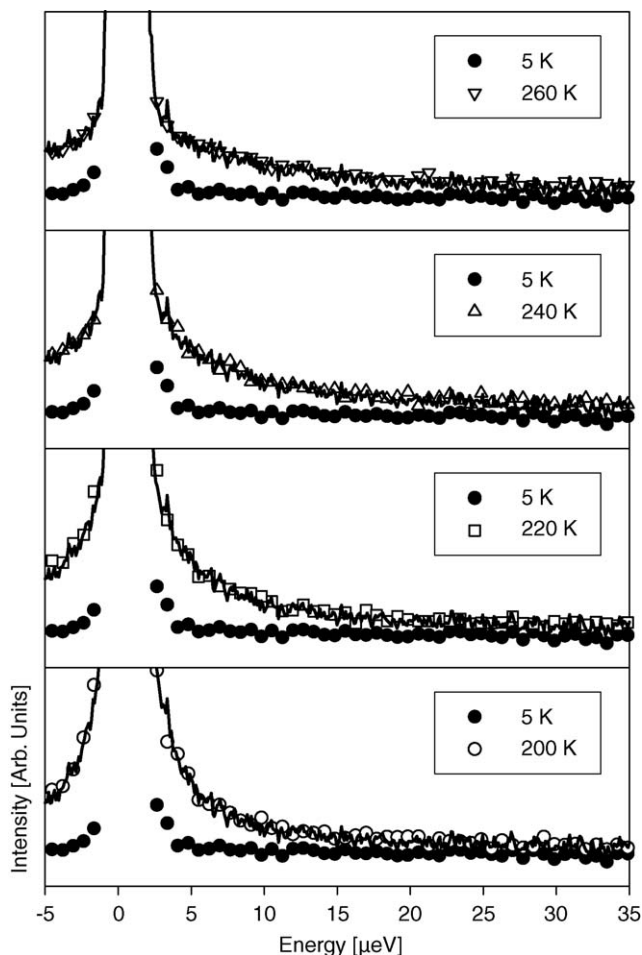


Fig. 2. Symbols: QENS spectra at $Q = 1.32 \text{ \AA}^{-1}$. The 5 K data represent the resolution function. Solid lines: fits obtained using Eqs. (1)–(5). The wiggles in the fits are due to convolution of the model scattering function with the experimentally measured resolution function that has wiggles. The energy transfer range and elastic peaks are truncated to emphasize the QENS signal.

describing the hopping between six sites on a circle of radius r [19] was modified to account for the immobile hydrogen atoms. Our previous work [11] has indicated that all H atoms in the o sites and some H atoms in the t sites are immobile on the time scale of the backscattering spectrometer and contribute to the elastic scattering. The fraction of the immobile H atoms in the t sites relative to all H atoms in the t sites is commonly described by a temperature-dependent parameter, $1-p(T)$. In stoichiometric hydrides such as $\text{Pr}_2\text{Fe}_{17}\text{H}_5$, some H atoms in the t sites may be trapped, for example, by anti-site defects in the host lattice. The resulting scattering function is given by

$$S(Q, E) = \left[\frac{3}{4} + \frac{1}{4}(1-p(T)) + \frac{1}{4}p(T)A_0(Q) \right] \delta(E) + \frac{1}{4}p(T) \left[A_1(Q) \frac{1}{\pi} \frac{\Gamma_1}{E^2 + \Gamma_1^2} + A_2(Q) \frac{1}{\pi} \frac{\Gamma_2}{E^2 + \Gamma_2^2} + A_3(Q) \frac{1}{\pi} \frac{\Gamma_3}{E^2 + \Gamma_3^2} \right] \quad (1)$$

$$A_0(Q) = \frac{1}{6} [1 + 2j_0(Qr) + 2j_0(Qr\sqrt{3}) + j_0(2Qr)] \quad (2)$$

$$A_1(Q) = \frac{1}{6}[2 + 2j_0(Qr) - 2j_0(Qr\sqrt{3}) - 2j_0(2Qr)] \quad (3)$$

$$A_2(Q) = \frac{1}{6}[2 - 2j_0(Qr) - 2j_0(Qr\sqrt{3}) + 2j_0(2Qr)] \quad (4)$$

$$A_3(Q) = \frac{1}{6}[1 - 2j_0(Qr) + 2j_0(Qr\sqrt{3}) - j_0(2Qr)] \quad (5)$$

where j_0 is the spherical Bessel function of 0th order, and the Lorentzian half widths at half maximum (HWHM) are functions of the time between jumps, τ : $\Gamma_1 = 0.5 \times (\hbar/\tau)$, $\Gamma_2 = 1.5 \times (\hbar/\tau)$, $\Gamma_3 = 2.0 \times (\hbar/\tau)$. Eqs. (1)–(5) are similar to those previously used for $\text{Pr}_2\text{Fe}_{17}\text{H}_5$ [11], except for the coefficients in Eq. (1) reflecting the fact that the H atoms in the t sites account for two-fifths and one-fourth of the total hydrogen content in $\text{Pr}_2\text{Fe}_{17}\text{H}_5$ and $\text{Pr}_2\text{Fe}_{17}\text{H}_4$, respectively. When fitting to the data, the scattering function described by Eq. (1) was convolved with the instrument resolution function. We used two fitting parameters, $p(T)$ and τ , and a fixed value of $r = 1.16 \text{ \AA}$ because, for six equidistant sites on a circle, the distance between two neighboring sites is equal to the circle radius. At each temperature, the fitting parameters were calculated by means of averaging the parameters obtained from individual fits at nine Q values.

Figs. 3 and 4 show the comparison of the fitting parameters obtained for $\text{Pr}_2\text{Fe}_{17}\text{H}_5$ [11] and $\text{Pr}_2\text{Fe}_{17}\text{H}_4$ (this work). The temperature dependence of the residence time between jumps for $\text{Pr}_2\text{Fe}_{17}\text{H}_4$ can be fit with an Arrhenius-type law with an activation energy of 0.10 eV. For $\text{Pr}_2\text{Fe}_{17}\text{H}_5$, the activation energy of 0.14 eV was obtained using the data collected at 200, 220, 240, and 260 K on the HFBS and at 390 K on a cold neutron time-of-flight spectrometer. Using only the data collected on the HFBS to obtain the activation energy for $\text{Pr}_2\text{Fe}_{17}\text{H}_5$ as shown in Fig. 3 provides a more direct comparison between the measurements of $\text{Pr}_2\text{Fe}_{17}\text{H}_4$ and $\text{Pr}_2\text{Fe}_{17}\text{H}_5$ and yields an activation energy of 0.12 eV for $\text{Pr}_2\text{Fe}_{17}\text{H}_5$. In either case, the activation energy for $\text{Pr}_2\text{Fe}_{17}\text{H}_5$ is not dramatically higher compared to that for $\text{Pr}_2\text{Fe}_{17}\text{H}_4$. As we have suggested previously [11], only the correlated jumps in the same direction that keep the H atoms on the opposite vertices of the hexagon should be possible, whereas uncorrelated jumps that place the H atoms within a distance

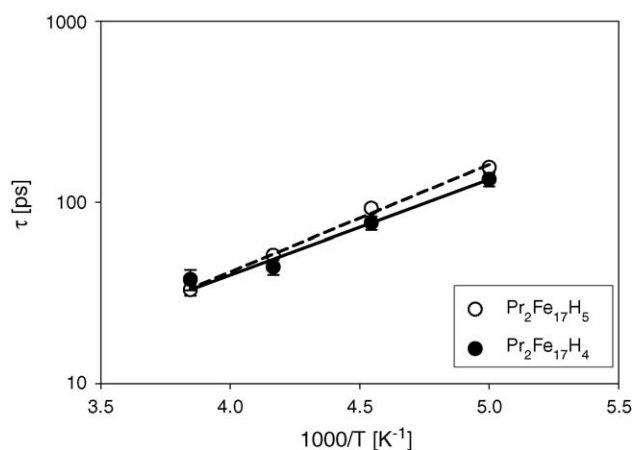


Fig. 3. Arrhenius fits of the temperature dependence of the residence time between jumps for $\text{Pr}_2\text{Fe}_{17}\text{H}_4$ (this work, solid line fit) and $\text{Pr}_2\text{Fe}_{17}\text{H}_5$ ([11], dashed line fit). For $\text{Pr}_2\text{Fe}_{17}\text{H}_5$, only the data obtained at the backscattering spectrometer were used for the fitting.

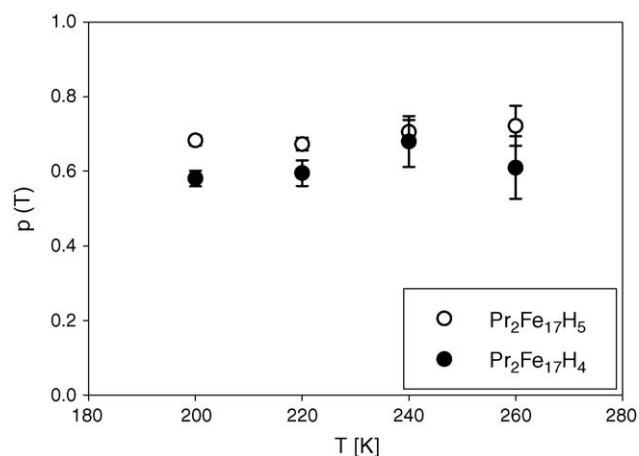


Fig. 4. The temperature dependence of $p(T)$ (the mobile fraction of hydrogen atoms in the tetrahedral sites) for $\text{Pr}_2\text{Fe}_{17}\text{H}_4$ (this work) and $\text{Pr}_2\text{Fe}_{17}\text{H}_5$ [11].

from each other where repulsive H–H interactions are appreciable do not take place. With a weaker H–H repulsive interaction allowing the placement of hydrogen atoms not necessarily on the opposite vertices of a hexagon, a stronger influence of the extra hydrogen atoms on the activation energy of the hopping process could be expected.

Fig. 4 demonstrates that, at each of the measured temperatures, the fraction of mobile H atoms in the tetrahedral sites is slightly lower for $\text{Pr}_2\text{Fe}_{17}\text{H}_4$ compared to $\text{Pr}_2\text{Fe}_{17}\text{H}_5$. The fact that removing one-half of hydrogen atoms from the t sites does not appreciably increase the fraction of mobile H atoms is consistent with our earlier hypothesis [11] that the immobilization of some atoms in the t sites occurs due to the defects in the host metal lattice rather than H–H interactions. These defects in the $\text{Pr}_2\text{Fe}_{17}$ lattice apparently render some hexagons “unsuitable” for hydrogen hopping. The closeness of the parameter $p(T)$ for the two compositions suggests that both the “suitable” and “unsuitable” hexagons for H hopping in $\text{Pr}_2\text{Fe}_{17}\text{H}_4$ are filled with H atoms with approximately equal probability. Preferential filling of the “suitable” hexagons would result in $p(T)$ being higher for $\text{Pr}_2\text{Fe}_{17}\text{H}_4$, whereas preferential filling of the “unsuitable” hexagons would yield a higher value of $p(T)$ for $\text{Pr}_2\text{Fe}_{17}\text{H}_5$.

4. Conclusions

We have investigated the hopping dynamics of hydrogen atoms in $\text{Pr}_2\text{Fe}_{17}\text{H}_4$, where three hydrogen atoms per formula unit fully occupy the 9e distorted o sites of the host metal lattice, and one hydrogen atom per formula unit fills one sixth of the 18g t sites. We have observed the hopping of the hydrogen atoms between such t sites that constitute arrays of isolated hexagons in the basal plane perpendicular to the c -axis. The residence time of H atoms between jumps shows an Arrhenius-type temperature dependence with an activation energy of 0.10 eV, which is only about 20% lower compared to that in $\text{Pr}_2\text{Fe}_{17}\text{H}_5$, where each hexagon is occupied by a pair of hydrogen atoms. This finding is consistent with our previous assertion that the jumps of the paired H atoms on a hexagon in $\text{Pr}_2\text{Fe}_{17}\text{H}_5$ are correlated; that is, only the simultaneous jumps of two atoms in the same direction

occur. In such a scenario, the direct H–H repulsive interaction between the atoms constituting a pair on a hexagon prohibits uncorrelated jumps, and, therefore, has only minor influence on the activation energy for the correlated jumps. The small increase in the hopping activation energy in $\text{Pr}_2\text{Fe}_{17}\text{H}_5$ compared to $\text{Pr}_2\text{Fe}_{17}\text{H}_4$ is likely due to an increased lattice constant and the interactions of extra t-site hydrogen atoms with the metal atoms of the host lattice. Additionally, we have found only a small difference between $\text{Pr}_2\text{Fe}_{17}\text{H}_4$ and $\text{Pr}_2\text{Fe}_{17}\text{H}_5$ in the fraction of H atoms immobilized in the t sites, which tends to be slightly higher in $\text{Pr}_2\text{Fe}_{17}\text{H}_4$. This is in agreement with our earlier hypothesis [11] that such an immobilization is due to defects in the host metal lattice, which make some hexagons “unsuitable” for hydrogen hopping, rather than direct H–H interactions. This also suggests that both the “suitable” and “unsuitable” hexagons for H hopping in $\text{Pr}_2\text{Fe}_{17}\text{H}_4$ are filled with H atoms with approximately equal probability.

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